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(54) Title: LOW VOC POLYOL ALKYD DISPERSION AND POLYURETHANE DISPERSIONS

(57) Abstract: Disclosed is a method for the preparation of stable, fine particle size and low volatile organic compound (VOC) content, aqueous dispersions of polymer. Low VOC waterborne polyol alkyd dispersions (PADs) and alkyd polyurethane dispersions (PUDs) can be obtained by this method. The alkyd polyurethane dispersions (PUDs) are obtained from polyol alkyd dispersions (PADs) which are polyethylene glycol (PEG) modified and solvent free. Polyurethane dispersions (PUDs), which are stable and have low VOC can be obtained by the reaction of a di-isocyanate (IPDI) with the alkyd dispersion and applied in one pack (1K) coating system. Waterborne polyol alkyd dispersion (PADs) can also be applied in two pack (2K) coating system by reacting with polyisocyanate or other crosslinkers to give low VOC waterborne coating systems. Coatings comprising polyurethane dispersions, having low VOC content, may be used on the surface of objects made of metal, wood, glass or plastic.

## **"LOW VOC POLYOL ALKYD DISPERSIONS AND POLYURETHANE DISPERSIONS"**

THE PRESENT INVENTION relates to low volative organic compound (VOC) polyol alkyd dispersions and polyurethane dispersions, methods for their production, and coatings produced therefrom.

Under new environment standards and regulations, there is an increased interest in developing low or near-zero VOC coating systems. Waterborne polyurethane coatings are an important part of this new development effort. Waterborne polyurethane dispersions are non-toxic, non-flammable and do not pollute air or water, and they have potential for use in the coatings industry. As polyurethane coatings have advantageous properties, such as superior abrasion resistance, toughness, chemical resistance, corrosion resistance and a wide range of mechanical strengths, they have attracted more attention than other systems.

Conventionally, dispersions are obtained by incorporation of an ionic group from a salt (ionomer dispersion), and/or a hydrophilic side group, into the polymer structure. Most of the current commercial polyurethane dispersions (PUDs) coating systems are prepared by one of the following two approaches. Either the polyurethane is polymerized in a solvent, then dispersed in water; or an isocyanate-terminated pre-polymer is prepared in a melt or in an aprotic solvent, and is then chain extended with a diamine in the water phase, in the

presence of a neutralizing tertiary amine, (J. Polym. Sci., Polym. Chem., 1996, Vol 34, 1095-1104).

More generally, four main methods have been used to produce stable dispersions:-

Firstly, the acetone process (US 4820762) is widely used in preparing polyurethane dispersions, wherein the polyurethane polymer is synthesized as a solution in acetone. After thinning with water, the organic solvent is distilled off, with the hydrophobic polymer being precipitated during distillation. As a suitable counter ion must be added to ensure the stability of the dispersion as it forms, some co-solvent and surfactant must be added, making it difficult to lower the VOC content in the final coating system. Although this process is suitable for reliably producing a broad range of chemical structures of PUDs, it can only be used to produce PUDs which are soluble in acetone. Consequently, the resulting polyurethane paint films are not very solvent resistant.

Secondly, the ketimine and ketazine process (US 4009307) can yield high quality polyurethane dispersions by dispersing hydrophilic isocyanate (NCO) prepolymers with polyketimine or ketazines in water. The effect of water on the blocked amine within the dispersion results in homogeneous extension of the amine chain to form polyurethaneurea.

Thirdly, in the prepolymer mixing process, a hydrophilically modified prepolymer is mixed with water, then reacted with a diamine. If the reaction is controlled carefully, the reaction of the NCO groups with the diamine dominates over the reaction with water. In order to control the viscosity of the

prepolymer, a small amount of solvent must be added, which remains as a co-solvent in the dispersion.

Lastly, in the hot melt process, the polyurethane prepolymer is synthesized in low solvent content medium. This process can ensure a suitable viscosity of the polyurethane prepolymer, which can make dispersion and chain extension proceed smoothly. However, it is subject to the compatability of the polyurethane prepolymer with water and chain extender, and usually requires the use of some co-solvent and surfactants to achieve a stable dispersion.

The particle size of the dispersions obtained from the above processes is related to the stirring rate.

The present invention seeks to provide stable, low VOC, polyethylene glycol (PEG) modified, aqueous polyol alkyd dispersions (PADs) which can be used in two component (2K) coating systems, and also aqueous polyurethane dispersions (PUDs) which can be used in one component (1K) coating systems, and their methods of production.

In particular, the present inventions seeks to provide a new method for the preparation of low VOC polyurethane dispersions combining ionic and non-ionic groups into the polymer structure, and also products that can be self-emulsified without co-solvent and external stabilizers, to form stable dispersions.

Furthermore, the present invention seeks to provide a simple and efficient method for the preparation of polyurethane dispersions, especially on a large scale, and also to provide polyurethane dispersion coatings, paint and binder compositions which possess a wide range of properties including solvent

resistance, good adhesion, hardness, flexibility, scrub resistance, and good color retention.

The present invention has the following advantages:

- 1) The invention allows the use of polyethylene glycol (PEG) in the preparation of alkyd resins. Using PEG in alkyd resin synthesis allows a combination of ionic and non-ionic groups into the polymer structure. The resultant resin may be self-emulsified, without co-solvent and external stabilizers, to form stable polyol alkyd dispersions. In particular, low VOC (<50g/l) aqueous dispersions may be obtained.
- 2) The PEG-modified PADs of the present invention exhibit good reactivity with some crosslinkable monomers and polymers, and may be used in 1K or 2K coating systems. As these dispersions and their derivative products have low VOC content (<50g/l), they can meet increasingly stringent government regulations on VOC and thus have great commercial value.
- 3) The PADs of the present invention and their similar products can also be used in processes of making low VOC baking-type coating systems and non-isocyanate (NCO group free) crosslinking type coating systems.
- 4) The process of making low VOC PADs of the present invention can also be applied in making low VOC polyester dispersions which can be used in making a wide range of low VOC coating systems.
- 5) The low VOC PADs of the present invention and their similar products, are stable over a wide range of temperatures (from 20° to 35°C) and pH (from pH 6.5 to 9.0).

6) The dispersion process of the present invention can also be applied to prepare low VOC aqueous dispersions containing ionic and non-ionic groups in the polymer structure.

These objectives and advantages may be achieved by the application of the present invention using solvent-free and PEG modified polyol alkyd dispersions and their derivative products, to produce polyurethane dispersions with excellent properties.

According to the present invention there is provided a method of making a polyol alkyd resin comprising an alcoholysis step of reacting polyethylene glycol (PEG), an oil and a polyhydroxy compound; followed by an esterification step of reacting the resultant mixture from the alcoholysis step with an acid and/or an acid anhydride, and a polyhydric alcohol with the esterification step being terminated on reaching a predetermined acid value or predetermined viscosity.

Preferably the oil is safflower oil.

Conveniently the oil is soybean oil.

Advantageously the polyhydric alcohol and/or the polyhydroxy compound is pentaerythritol.

Preferably the acid is p-t-butyl benzoic acid or benzoic acid.

Advantageously, the acid is, or the acid anhydride corresponds to, a polybasic acid.

Preferably, the acid is isophthalic acid.

Conveniently the acid anhydride is phthalic anhydride.

Advantageously the PEG has a molecular weight in the range of 3000-3700.

According to another embodiment of the present invention there is provided a polyol alkyd resin.

According to a further embodiment of the present invention there is provided a method of making an aqueous polyol alkyd resin dispersion, (PAD), comprising the steps of heating in a reactor a predetermined amount of water, and a predetermined amount of an amine, to a dispersing temperature, and pouring into the reactor, with stirring, a polyol alkyd resin, which has been heated to a melt state, at such a rate that the temperature of the mix in the reactor is no more than about 5°C above the dispersing temperature, with the temperature in the reactor being held at about the dispersing temperature for a period of time after the addition of the resin.

Conveniently, the method further comprises the step of cooling the mix to room temperature and adjusting the pH and/or solids content of the dispersion.

Preferably the amine is triethylamine, 2-amino-2-methyl-1-propanol, dimethylethanol amine (DMEA) or ammonia solution.

Conveniently the dispersing temperature is in the range of 55°-70°C.

Advantageously the dispersing temperature is in the range of 60°-65°C.

Preferably the amine is added in a mole ratio amount in the range of 0.3-1.0:1.0 with respect to the resin.

Conveniently the amine is added in a mole ratio amount in the range of 0.6-0.95:1.0 with respect to the resin.

Advantageously the solids content of the dispersion is in the range of 35-45%.

Preferably the solids content of the dispersion is in the range of 38-40%.

According to another embodiment of the present invention there is provided an aqueous polyol alkyd resin dispersion, (PAD).

According to a further embodiment of the present invention there is provided a method of making an aqueous polyurethane dispersion (PUD) from a polyol alkyd dispersion (PAD) comprising the steps of heating in a reactor a predetermined amount of water, and a predetermined amount of an amine, to a dispersing temperature, and pouring into the reactor, with stirring, a polyol alkyd resin, which has been heated to a melt state, at such a rate that the temperature of the mix in the reactor is no more than about 5°C above the dispersing temperature, with the temperature in the reactor being held at about the dispersing temperature for a period of time after the addition of the resin, followed by reaction with an isocyanate chain extender.

Conveniently, the method further comprises the step of cooling the mix to room temperature and adjusting the pH and/or solids content of the dispersion.



Preferably the amine is triethylamine, 2-amino-2-methyl-1-propanol, dimethylethanolamine (DMEA) or ammonia solution.

Conveniently the dispersing temperature is in the range of 55°-70°C.

Advantageously the dispersing temperature is in the range of 60°-65°C.

Preferably the amine is added in a mole ratio amount in the range of 0.3-1.0:1.0 with respect to the resin.

Conveniently the amine is added in a mole ratio amount in the range of 0.6-0.95:1.0 with respect to the resin.

Advantageously the solids content of the dispersion is in the range of 35-45%.

Preferably the solids content of the dispersion is in the range of 38-40%.

Conveniently the chain extender is an isocyanate-containing compound.

Advantageously the isocyanate-containing compound is an aliphatic compound.

Preferably the isocyanate-containing compound is isophorone di-isocyanate.

Conveniently the isocyanate-containing compound is an aromatic compound.

Advantageously the isocyanate containing compound is a di-isocyanate.

Preferably the chain extender is an aziridine-containing compound.

Conveniently the range of equivalents of the chain extender to the solids content of the polyol alkyd dispersion is in the range of between 10:90 and 30:70.

Advantageously the range of equivalents of the chain extender to the solids content of the polyol alkyd dispersion is in the range of between 10:90 and 20:80.

Preferably the range of equivalents of the chain extender to the solids content of the polyol alkyd dispersion is about 15:85.

Conveniently the reaction is performed in the temperature range of from about 25°C to about 30°C.

According to another embodiment of the present invention there is provided an aqueous polyurethane dispersion, (PUD).

According to a further embodiment of the present invention there is provided a one component (1K) or a two component (2K) coating system comprising the dispersion of the present invention.

Preferably the coating system is a room temperature cure or a baking-type coating system.

According to another embodiment of the present invention there is provided a film made from the dispersion of the present invention.

In order that the invention may be more readily understood, and so that further features thereof may be appreciated, the invention will now be described, by way of example, with reference to the accompanying drawings in which:

FIGURE 1 is a graph showing the stability of viscosity with time for examples of PADs;

FIGURE 2 is a graph showing the change in viscosity with time for the examples of PADs of Figure 1;

FIGURE 3 is a graph showing the change in pH over six months for examples of PUDs;

FIGURE 4 is a graph showing the change in viscosity over six months for the examples of PUDs of Figure 3;

FIGURE 5 is a graph showing the change in pH over six months for further examples of PUDs; and

FIGURE 6 is a graph showing the change in viscosity over six months for the further examples of PUDs of Figure 5.

The present invention is directed to methods of making stable low VOC (<50g/l) waterborne polyol alkyd dispersions (PADs). One type of low VOC waterborne polyol alkyd dispersions is obtained by dispersing a polyethylene glycol (PEG) modified, solvent-free, alkyd resin which contains certain chemical structures. This kind of polyol alkyd dispersion can react with diisocyanates to give stable, fine particle size and low VOC polyurethane dispersions which can be applied as 1K binders in coating systems. The polyol

alkyd dispersions also can be crosslinked by reaction with polyisocyanates, polyfunctional aziridines and other crosslinkers to give low VOC binders in 2K coating systems.

The invention also has the advantages of using PEG as a non-ionic part of raw materials for making alkyd dispersions; using isophorone diisocyanate as a reactant to obtain 1K waterborne PUD systems; and using an aliphatic polyisocyanate as a crosslinker to achieve 2K waterborne PUD finishings.

The invention also relates to coatings making use of these dispersions. Coatings made from these dispersions are particularly suitable for uses on surfaces such as wood, metal, glass, plastic and other substrates where traditional solvent-based polyurethanes are used.

The alkyd resin of the present invention is a PEG modified solvent free, short oil alkyd resin with certain chemical structures. The term "short oil" denotes a level of less than 40% oil in solids. The alkyd dispersion (PAD) is prepared by dispersing the above resin in water with an amine neutralizer in the absence of other solvents. This process produces a stable, fine particle size and low VOC content (<50 g/l) waterborne polyol alkyd dispersion.

The waterborne polyurethane dispersions (PUDs) for 1K system are obtained by performing a urethane reaction of a polyol alkyd dispersion (PAD) with a di-isocyanate. The waterborne polyurethane dispersions (PUDs) for 2K system are obtained by crosslinking the polyol alkyd dispersion (PAD) with a polyisocyanate or other crosslinker.

In the case of an isocyanate, the amount of cross-linker may be calculated by the following formula:

$$\begin{array}{l} \text{Isocyanate cross-linker needed} \\ \text{for equivalence of 100 pbw OH resin} \end{array} = \frac{247 \times (\% \text{OH in resin})}{\% \text{NCO in isocyanate resin}}$$

The resultant dispersions have low VOC content (<50 g/l) and fine particle size, are cosolvent-free, and surfactant-free, and are physically and chemically stable.

The solvent-free alkyd resin is prepared from monomers by a two step process; alcoholysis, followed by esterification. A small amount of solvent (for example, butyl cellosolve) is helpful in the first step of reaction, and is stripped off at the second step of the reaction. Termination of the reaction is controlled by achieving an predetermined acid value and viscosity. The reaction time and temperature for obtaining the proper degree of alcoholysis in the first step is about 3 hours at 250°C. In the second step, the esterification is carried out at 230°C.

An example of reaction components and procedures is shown in Table 1.

Table 1

No.	Component
#1	REFINED SAFFLOWER OIL PEG p-t-BUTYL BENZOIC ACID PENTAERYTHRITOL BUTYL CELLOSOLVE LITHIUM HYDROXIDE MONOHYDRATE DE-IONIZED WATER
#2	PENTAERYTHRITOL PHTHALIC ANHYDRIDE ISOPHTHALIC ACID

### Procedure

1. Charge #1 into a synthesis reactor equipped with agitator, sample tube, thermometer, nitrogen purge, decanter and condenser. Heat the reactor to perform alcoholysis.
2. After achieving the proper degree of alcoholysis, cool the reactor to the desired temperature before charging #2. Then heat up the reactor again to carry out esterification. Terminate the reaction after achieving the predetermined acid value and viscosity.

The raw materials requirements for the resin may include the following:

ALCOHOLS: pentaerythritol, glycerine, trimethylol propane, trimethylol ethane, ethylene glycol, neopentyl glycol, propylene glycol, cyclohexanedimethanol,

ACIDS AND ACID ANHYDRIDES: benzoic acid, p-t-butyl benzoic acid, capric acid, castor fatty acid, coconut fatty acid, dimethylol propionic acid, 2-ethyl butyric acid, lauric fatty acid, linseed fatty acid, myristic acid, oleic acid, palargonic acid, soya fatty acid, stearic acid, tall oil fatty acid, adipic acid, azelaic acid, fumaric acid, isophthalic acid, maleic anhydride, phthalic anhydride, terephthalic acid, trimellitic anhydride,

OILS: soybean oil, castor oil, coconut oil, dehydrated castor oil, linseed oil, safflower oil, tung oil.

The molecular weight of the PEG is preferably from 3000 to 3700. Safflower oil and soybean oil are both suitable for the reaction, but safflower oil is preferred. Benzoic acid, which is usually used in alkyd preparation, can also be applied in this alkyd resin, but p-t-butylbenzoic acid is preferred.

The preferred specifications of the alkyd resin are listed in Table 2.

Table 2

1	Non-Volatile Matter (NVM), 110°C, 1 hr (ASTM D-1259)	100 %
2	Colour (60% in Xylene) (ASTM D-1544)	3-5
3	Viscosity (60% in Xylene) (ASTM D1545)	X-Z
4	Acid Value (AV) (ASTM D1639)	12±1; 15±1; 20±1

The color and viscosity of alkyd resin at 60% in xylene may range from 3 to 7 for color and from V to Z5 for viscosity, but preferably with the range from 3 to 5 for color, and X to Z for viscosity. The acid value of the alkyd resin may range from 12 to 25, but preferably within the range from 12 to 15. The molecular weight (Mw) of the resins typically range from about 3,000 up to 14,000, but preferably within the range from 4,000 to 10,000. High molecular weight resins tend to be very viscous and difficult to disperse.

During storage, the alkyd resins exhibit good stability, and are ready to use. As storage time increases (more than 1.5 months), the surface of resin might form an elastic membrane. This membrane may originate from the air-oxidation of the resin, and will affect the quality of the subsequent alkyd dispersion. In order to minimize this effect on the dispersing process, it is preferable to discard the membrane.

Polyol alkyd dispersions are prepared by pouring a pre-heated alkyd resin into water with mild stirring. A general procedure is discussed below.

The alkyd resin is heated to a melt state. Meanwhile, the calculated amount of de-ionized water is heated to the dispersing temperature in an emulsion reactor fitted with an anchor stirrer. (The amount of water is based on the desired NVM% of the final product).

A calculated amount of an amine (for example triethylamine, TEA), is added to the reactor with efficient stirring. The heated resin is then added to the emulsion reactor at such a rate that the temperature of the emulsion reactor is no more than about 5°C above the dispersing temperature.

The amount of amine may be calculated as follows:

$$A = R(AN)E / 56,100$$

A = weight of amine

R = weight of total resin solids

AN = acid number (solids)

E = equivalent weight of amine.

After complete addition of the resin, the emulsion reactor is maintained at about the dispersing temperature for some time in order to cure the dispersion. The reactor is then cooled to room temperature, the pH adjusted to neutral and the solids content adjusted to the required value. Characteristics of the resulting dispersion are shown below:



Appearance	Milky white
Non-Volatile Matter (NVM) 110°C, 1 hr	35-45%
Viscosity (Brookfield, S63, 60rpm)	300-1800 CPS
Specific Gravity	1.04-1.07
VOC (g/l)	<50
Particle Size	<5 $\mu$ m
pH	6.5-8.5

No high-speed agitation is needed for the alkyd dispersion formation. Typically, a pre-heated alkyd resin is added to a mixture of water and amine, at 55-70°C, with mild stirring, in an amount sufficient to obtain a dispersion of about 35-45 weight percent solids, following by curing, and adjustment of the pH to a desired value to obtain a suitable viscosity. Triethylamine, 2-amino-2-methyl-1-propanol, dimethylethanol amine (DMEA) and ammonia solution can be used as neutralizing reagents, (AMP95 is proprietary 2-amine-2-methyl-1-propanol supplied by ANGUS Chemie GMBH). The amount of neutralizer used during the dispersing process is in the range of 0.3-1.0:1.0 (mole ratio), more preferably in the range of 0.6-0.95:1.0. The particle size, and particle size distribution (PSD), may be measured using light diffraction techniques known in the art.

The general and preferable reaction conditions for alkyd dispersion (PADs) formation are shown below in Table 3:

No.	Process	Conditions	
		Generally	Preferably
1	Alkyd Resin pre-process	140°C 1 to 1.5 hr	140°C 1 hr
2	Alkyd Resin added rate	50 min-70 min	60 min
3	Stir rate	80-180 rpm	120-140 rpm
4	Temperature	55-70°C	60-65°C
5	NVM%	35-45	39 $\pm$ 1
6	First added amine ratio	0.3-1.0 : 1	0.6-0.95:1
7	Amine used	AMP 95, TEA; ammonia solution	AM95 or TEA
8	Final product pH	Adjust to 6.5-8.5	Adjust to 7-7.5

The obtained alkyd dispersions have excellent storage stability and a solid content of about  $39\pm 1\%$  by weight. The particle size is generally smaller than 5 micron, preferably from 0.01 to 1.0 micron. The small particle size enhances the stability of the dispersed particles and also leads to the production of films with high surface gloss.

The alkyd dispersions (PADs) have good stability in particle size of over 6 months at room temperature. However, the pH value and viscosity of the dispersions decrease as the storage period is prolonged.

With prolonged storage time, separation was observed from the homogenous alkyd dispersion, but the separation can be easily reversed with efficient stirring.

The polyol alkyd dispersions (PADs) of the present invention can be reacted with a di-isocyanate, such as isophorone diisocyanate (IPDI), to give stable, fine particle size, and low VOC content waterborne polyurethane dispersions (PUDs).

Preferably, the range of equivalents of isophorone di-isocyanate (IPDI) to the solids of the alkyd dispersions ratio is between 10:90 and 30:70, more preferably 10:90, 15:85, and 20:80.

The recommended optimal temperature range for PUD preparation in the method of the present invention is between 25 and 30°C.

The polyurethane dispersions (PUDs) of the present invention have relatively good appearance stability at room temperature. After 6 months of storage, the

PUDs exhibit good stability in particle size, with only a slight increase in pH value and a slight decrease in viscosity.

The polyol alkyd dispersions (PADs) can be crosslinked by reaction with crosslinkers to give a type of low VOC binders in 2K coating systems. The crosslinkers used in 2K systems may be aliphatic or aromatic polyisocyanates, aliphatic polyisocyanates, polyfunctional aziridines or other crosslinkers.

The method of making low VOC polyol alkyd dispersions of the present invention can also be applied to make low VOC polyester dispersions that can be applied to make a wide range of low VOC coating systems.

The polyol alkyd dispersions (PADs) of the present invention and their similar products can also be used in processes of making low VOC baking type coating systems and non-isocyanate (NCO group free) crosslinking type coating systems.

Films can be made from these dispersions by methods known in the art. Thus, the dispersions could be formulated with other components to achieve desired properties of the coating systems and also to obtain desired film properties. The dispersions can be applied by casting, spraying, brushing or rolling. The PUD coatings can be used on wood, glass, metal, plastic and other surfaces.

Some interesting results were obtained in clear coats prepared from the waterborne alkyd 1K PUD system of the present invention with the end products having a range of appearances. The gloss of clear coats is reduced as the PUD content is increased, with a low percentage of PUD (PUD-11-1) resulting in higher gloss. On the contrary, a high percentage of PUD (PUD-11-

3) results in lower gloss. These type of 1K PUDs show good pigment dispersion when used in white coating systems.

In low VOC waterborne alkyd 2K polyurethane, the polyol alkyd dispersions performed very well when cross-linked with polyisocyanate. The resultant film has excellent gloss, good DOI, excellent flow and levelling, and good solvent resistance properties.

The following examples illustrate the present invention:

#### I. Preparation of Solvent-free Short Oil Alkyd Resin.

These examples show the general procedure for preparation of PEG-modified solvent free alkyd resins. The raw materials are listed below in Table 4:

Table 4

No.	Raw Materials	Amount, grms	%
#1	SAFFLOWER OIL	377.100	24.12
	PEG 3350	128.600	8.23
	p-t-BUTYL BENZOIC ACID	268.700	17.19
	PENTAERYTHRITOL	222.500	14.23
	BUTYL CELLOSOLVE	10.100	0.65
	LITHIUM HYDROXIDE MONOHYDRATE	0.2544	0.016
	D.WATER	0.310	0.027
#2	PENTAERYTHRITOL	130.800	8.31
	PHTHALIC ANHYDRIDE	318.600	20.38
	ISOPHTHALIC ACID	106.200	6.79
Water/solvent, Loss		99.500	
Product		1463.664	93.63
Total		1563.164	100

#### A. Alcoholysis

Charge #1 into a 2-L flask equipped with agitator, sample tube, thermometer, nitrogen purge, decanter and condenser. Heat the reactor to 250°C, and then hold the reaction temperature at 246 to 253°C for 3 hrs. Cool the reactor to 170°C.

#### B. Esterification

Cool the reactor to 170°C and add #2, then heat the reactor to 230°C, and hold the reaction temperature at 227-233°C for 1 h for the first sampling, then start sampling every 20 mins. Hold at 228°C until a predetermined acid value and viscosity at 60% solid in xylene are reached.

Table 5 presents some properties of alkyd resins prepared according to this method. (The molecular weight of the polymers is measured using Gel Permeation Chromatography, GPC).

Table 5 (Resin:PC-PUD-01(Alkyd Base))

RWA-1194, AV~12										RWA-1196, AV~25						RWA-1185, AV~15	
Batch No.	001	002	003	004	005	006	008	001	002	003	004				001		
Weight (g)	1350	3125	1313	1330	1979		2346	1350	3196	3200	1999				1990		
Specifications																	
NVM%	100	100	100	100	100	100	100	100	100	100	100	100	100	100			
AN (solid)	12.55	12.7	12.66	12.17	11.83	13.0	12.2	24.77	24.9	25.55	24.0			15.67			
Colour (60% in xylene)	8	4-	5+	6-7	5-6	5-6	5	3+	5-	5+	6			5-6			
Viscosity (60% in xylene)	Z-	Z+	Z-2+	Z3/4	X+3/4	V	Z+1/2	W+1/2	X+	X+1/2	X			X			
Mw	9075	7147	9247	12485	14228	10079	10528	4068	4350	4183	4640			7966			

Resin: PC-PUD-01(Alkyd Base)

RWA-1195, AV~20												
Batch No.	001	002	003	004	005	006	007	009	010	013	014	
Weight (g)	1350	3192	3205	3200	1417	1442	1432	2067	3227	2050	2200	
Specifications												
NVM%	100	100	100	100	100	100	100	100	100	100	100	
AN (solid)	21.35	20.17	19.87	20.45	19.0	20.67	20.83	20.67	20.75	19.33	20.5	
Colour (60% in xylene)	3	6	3+	4+	6	6-7	7	5-6	6+	4	4-5	
Viscosity (60% in xylene)	X+	Y+	Y-	Y+1/2	X-Y	Z1	Y	Y+1/2	Y+	W+1/ 4	X	
Mw	7701	5913	5680	8428	7557	6012		11084	5569	6566	4862	

## II. Preparation of Low VOC Waterborne Alkyd Dispersion (PADs).

Alkyd dispersions (PADs) are prepared by pouring a pre-heated alkyd resin into water with mild stirring. A typical procedure is show below. The general characteristics of the PADs are also displayed in Table 6.

A general procedure for preparing low VOC alkyd dispersion (PAD) (REA-1162) is discussed below:

Materials	Amount, grams
ALKYD RESIN {RWA-1194} (AV=12)	1500
DE-IONIZED WATER	2363.6
TRIETHYL AMINE	32.47
Solid Content (%NVM), 110°C, 1 hour	38.5%

Put the base resin in 140°C oven for 1 hour to obtain melt status.

Charge the calculated amount of de-ionized water into an emulsion reactor fitted with an anchor agitator. Heat the reactor to 60°C.

Charge the calculated amount of TEA into emulsion reactor, under stirring at 100-120 rpm.

Transfer the base resin to emulsion reactor at such a rate that the temperature of emulsion reactor is not higher than 65°C.

When the transfer is completed, hold the reactor at 60°C for 30 minutes with further stirring.

Cool the reactor to room temperature and adjust the pH of the emulsion to neutral and the solid content to the desired values.

Table 6 shows some physical properties of alkyd dispersions (PADs):



Table 6										
Alkyd Dispersions										
	REA-1162, AN~12			REA-1163, AN~15			REA-1165, AN~20			
Batch No.	001	009		001	001	001	002	004	006	008
Specifications										
NVM%	38.6	38.50		40.07	38.3		38.86	38.59	38.35	38.85
pH	7.16	7.06		7.06	6.82		7.04	7.58	7.29	7.19
Viscosity (s63, 60 rpm)	330	710		348	547		1010	882	1702	1320
Specific Gravity	1.05	1.04		1.057	1.056		1.056	1.056	1.04	1.056
Particle Size/PSD $\mu\text{m}$	0.516/0.357	2.733/1.530		3.106/1.179	2.605/1.467		3.182/1.812	1.065/1.535	4.283/1.884	0.095/0.106
VOC (g/l)	<50	<50		<50	<50		<50	<50	<50	<50

Alkyd Dispersions									
REA-1165, AN~20									
Batch No.	010	011	013	015	017	018	REA-1177,AN~20	REA-1167,AN~25	
Specifications									
NVM%	38.45	38.55	38.60	39.01	39.51	38.87	38.56	39.78	
pH	7.08	7.65	7.40	7.05	7.34	7.20	6.68	7.14	
Viscosity (s63, 60 rpm)	622	3040	620	1588	426	2472	1010		
Specific Gravity	1.056	1.056	1.059	1.057	1.054	1.055	1.061	1.053	
Particle Size/PSD μm	2.356/1.961	1.182/0.710	3.566/1.247	0.414/0.149	2.687/1.604	0.127/0.127	0.102/0.038	3.609/2.391	
VOC (g/l)	<50	<50	<50	<50	<50	<50	<50	<50	
Note							AMP 95 process		

### III. Preparation of 1K Polyurethane Dispersion (PUDs)

Examples of general procedures and ingredients for the preparation of 1K polyurethane dispersions (PUD) are shown below:

#### Formula for PUD-I system

PUD-I-1(PUD-07)		
Raw Materials	Amount, gms	Ratio of solid content (%)
Alkyd Dispersion (REA-1162-01)	95.89	90
IPDI	4.11	10
Total	100	100

PUD-I-2(PUD-08)		
Raw Materials	Amount, gms	Ratio of solid content (%)
Alkyd Dispersion (REA-1162-01)	93.62	85
IPDI	6.38	15
Total	100	100

PUD-I-3(PUD-09)		
Raw Materials	Amount, gms	Ratio of solid content (%)
Alkyd Dispersion (REA-1162-01)	91.20	80
IPDI	8.8	20
Total	100	100

PUD-I-4(PUD-10)		
Raw Materials	Amount, gms	Ratio of solid content (%)
Alkyd Dispersion (REA-1162-01)	88.60	75
IPDI	11.40	25
Total	100	100

Formula for PUD-II System

PUD-II-1(PUD-12)		
Raw Materials	Amount, gms	Ratio of solid content (%)
Alkyd Dispersion (REA-1165-01)	95.68	90
IPDI	4.32	10
Total	100	100

PUD-II-2(PUD-13)		
Raw Materials	Amount, gms	Ratio of solid content (%)
Alkyd Dispersion (REA-1165-01)	93.30	85
IPDI	6.70	15
Total	100	100

PUD-II-3(PUD-14)		
Raw Materials	Amount, gms	Ratio of solid content (%)
Alkyd Dispersion (REA-1165-01)	90.77	80
IPDI	9.23	20
Total	100	100

PUD-II-4(PUD-15)		
Raw Materials	Amount, gms	Ratio of solid content (%)
Alkyd Dispersion (REA-1165-01)	88.07	75
IPDI	11.93	25
Total	100	100

The calculated amount of alkyd dispersion (PAD:REA-1162 or REA-1165) is charged into an emulsion reactor with a thermocouple, agitator and kept efficiently stirred.

Add the IPDI to alkyd emulsion in 5-10 minutes at room temperature.

When IPDI is completely added, keep stirring for another 30 minutes at room temperature, then keep it and allow it to continue to react overnight.

Adjust the pH to 7.5-8.0 using ammonia solution and test the physical properties. The characteristics of the resulting PUDs are shown below in Tables 7, 8 and 9.

Table 7

PUD-I				
	PUD-I-1 PUD-07	PUD-I-2 PUD-08	PUD-I-3 PUD-09	PUD-I-4 PUD-10
Appearance	Milky White			
NVM% (110°C, 1h)	42.00	42.85	44.42	45.85
pH	7.60	7.59	7.65	7.62
Viscosity, CPS (Brookfield, S63, 60rpm)	78	84	146	328
Particle Size ( $\mu\text{m}$ )	0.772 13% 0.439 0.471 17% 0.143 0.51 70% 0.153	0.778 14% 0.453 0.447 24% 0.182 0.140 62% 0.141	0.789 18% 0.514 0.471 21% 0.144 0.164 61% 0.161	0.808 17% 0.593 0.471 19% 0.143 0.163 58% 0.159

Table 8

PUD-II				
	PUD-II-1 PUD-12	PUD-II-2 PUD-13	PUD-II-3 PUD-14	PUD-II-4 PUD-15
Appearance	Milky White			
NVM% (110°C, 1h)	42.95	44.35	46.18	47.39
pH	7.61	7.64	7.60	7.65
Viscosity, CPS (Brookfield, S63, 60rpm)	226	154	250	1120
Particle Size ( $\mu\text{m}$ )	2.879 94% 1.801 0.604 6% 0.263	2.443 90% 1.740 0.597 10% 0.282	2.435 87% 1.798 0.692 6% 0.162 0.487 7% 0.182	6.540 19% 4.249 3.127 51% 1.754

Table 9										
Polyurethane Dispersions (PUDs)						Reaction PADs				
PUD Type	Batch Code	NVM%	pH	Viscosity (CPS)	Particle Size $\mu\text{m}$	Batch code	pH	Viscosity (CPS)	Particle size/ PSD $\mu\text{M}$	PUD process time period
(IPDI% in PUD)										
1 (10%)	07-1	42.00	7.60	78	0.146/0.142	REA-1162-01	6.78	90	0.154/0.153	2 mn
	12-1	42.95	7.61	226	2.875/1.801	REA-1165-01	6.37	254	2.650/1.605	>2 mn.
	12-2	43.40	7.50	162	2.555/1.664	REA-1165-01	6.37	254	2.650/1.605	>2 mn
	12-3	41.07	7.23	228	0.926/0.773	REA-1165-03	7.10	758	2.565/2.016	1 w
2 (15%)	08-1	42.85	7.59	84	0.140/0.142	REA-1162-01	6.78	90	0.154/0.153	2 mn
	13-1	44.35	7.64	154	2.443/1.740	REA-1165-01	6.37	254	2.650/1.605	> 2 mn
	13-2	45.39	7.50	136	2.435/1.728	REA-1165-01	6.37	254	2.650/1.605	> 2mn
	13-3	42.62	7.16	284	0.926/0.777	REA-1165-03	7.12	492	2.565/2.016	2 w
3 (20%)	09-1	44.42	7.65	146	0.152/0.144	REA-1162-01	6.78	90	0.154/0.153	2 mn

14-1	46.18	7.60	250	2.435/1.798	REA-1165-01	6.37	254	2.650/1.605	>2 mn
14-2	46.27	7.51	178	2.411/1.830	REA-1165-01	6.37	254	2.650/1.605	>2 mn
14-3	44.53	7.02	462	2.471/2.230	REA-1165-02	6.96	732	3.052/1.574	2 w
14-4	44.28	6.63	690 (after 3 days)	0.214/0.247	REA-1165-04	7.23	492	0.090/0.139	>3 w
14-5-1	43.80	6.44	314 (after 4 days)	3.629/2.096	REA-1165-06	7.29	1702	4.283/1.884	0
14-5-2	44.40	5.76	52 (after 4 days)	6.416/3.629	REA-1165-06	4.99	22	6.896/3.355	0
14-5-3	44.40	6.19	54 (after 4 days)	5.568/3.509	REA-1165-06	5.38	46	6.841/3.457	0
14-6-1	44.12	6.78	746 (after 1 day)	0.102/0.107	REA-1165-08	7.18	1320	0.095/0.106	0
14-6-2	44.32	6.25	70 (after 1 day)	11.76/7.807	REA-1165-08	5.04	120	11.03/6.399	0
14-6-3	44.36	6.87	688 (after 4 days)	0.095/0.106	REA-1165-08	7.09	1274	0.080/0.091	1 w

	14-6-4	44.30	6.81	694	0.087/0.091	REA-1165-08	7.02	1260	0.089/0.106	2 w
4	10-1	45.85	7.80	328	0.167/0.143	REA-1162-01	6.78	90	0.154/0.153	2 mn
(25%)										
	15-1	47.39	7.65	1120	2.662/1.745	REA-1165-01	6.37	254	2.650/1.605	>2 mn
	15-2	47.99	7.50	448	2.597/1.862	REA-1165-01	6.37	254	2.650/1.605	>2 mn



#### IV Storage Stability Test

Each of the alkyd dispersions (PADs) and 1K alkyd polyurethane dispersions (PUDs) were examined for changes in viscosity, pH and particle size at room temperature for up to 6 months. Appearance stability of the dispersions of the present invention at room temperature and high temperature (50°C) were also tested, using the following methods:

##### Room temperature:

- a) Check appearance and test pH, viscosity and particle size of the dispersion every week for the first two months, and then every two weeks thereafter until 6 months. Record the time when the deposition of the dispersions appeared and when it cannot be reversed through efficiently stirring, and record the pH, viscosity and particle size data.
- b) Adjust the pH value of the dispersion to the fixed value and record the change of the status, viscosity and particle size of the dispersion every week for the first two months and then every two weeks thereafter until 6 months.

##### High temperature (50°C)

- a) Check appearance and test pH, viscosity and particle size of the dispersion every day. Record the time when the deposition of the dispersions appeared and when it cannot be reversed and record the pH, viscosity and particle size data.
- b) Adjust the pH value of the dispersion to the fixed value and record the change of status, viscosity and particle size of the dispersion every day until it cannot be recovered.

The results for a number of examples are shown below in Tables 10,11,12,13 and 14.

## IV-1. Alkyd dispersion (PAD)

Stability of particle size is shown in Table 10. During the 6 months of storage, there was no significant change of the particle size. However, the pH value and viscosity of dispersion decreased as the storage period increased.

**Table 10** Stability test of alkyd dispersion (PADs) over six months storage at room temperature {REA-1162-01, prepared: 24 Sept., 98; NVM% 38.6}.

Time (months)	Particle Size Data	pH Viscosity (CPS) *	pH Viscosity (CPS)
0	0.872 29% 0.589 0.463 21% 0.151 0.193 48% 0.164	7.16/330	
1 M	0.823 15% 0.586 0.461 18% 0.139 0.159 67% 0.156	7.03/	
2 M	0.830 13% 0.571 0.462 16% 0.140 0.154 71% 0.153	6.78/90	7.19/130
3 M	0.850 13% 0.653 0.463 16% 0.140 0.155 71% 0.153	6.56/92	7.18/98
4.5 M	0.534 41% 0.536;0.115.59% 0.112	6.36/50	
5 M	0.535 46% 0.553;0.117 54% 0.118	6.16/22	
6 M	0.946 9% 0.436;0.423 40% 0.209; 0.126 51% 0.121	5.95/28	
7 M	0.894 55% 0.413;0.114 45% 0.108	5.79/14	6.78/60

\* pH value not adjusted.

Table 11, Figure 1 and Figure 2 show viscosity change with respect to storage period at a fixed pH value, for examples of PADs, (alkyd dispersion (PADs): (REA-1165-02), A008EA).

Table 11

008E-1; pH 6.67			008E-2; pH 7.04			008E-3; pH 7.57			008E-4; pH 8.02		
Time (days)	pH	Visc. CPS	Time (days)	pH	Visc. CPS	Time (days)	pH	Visc. CPS	Time (days)	pH	Visc. CPS
0	6.67	310	0	7.04	1010	0	7.57	2160	0	8.02	5240
49	6.64	306	7	7.04	872	21	7.57	2596	21	8.04	5200
56	6.74	296	21	7.03	810	63	7.58	1956	91	8.06	5030
77	6.68	280	28	7.04	788	91	7.51	1826	105	8.07	5430
91	6.65	264	63	7.05	692	105	7.57	1952	133	8.40	3876
105	6.65	260	91	7.04	678	189	7.50	638	161	8.90	4850
133	6.62	156	105	7.05	732				189	8.84	2724
161	6.67	114	161	7.09	336						
189	6.69	100	189	7.14	288						

Table 12 shows the deposition formation time. The homogeneous status of alkyd dispersions (PADs) may be recovered through efficient stirring.

Table 12 The status change for alkyd dispersions {REA-1165-02, A008EA & REA-1167-01, A004EA}

Sample Code		pH Value	Viscosity (CPS)	Appearance	Deposit Appearance time (weeks)
REA-1165 #02	008E1	6.67	310	White	~2w
	008E2	7.04	1010	↓	~9w
	008E3	7.57	2160	↓	>13w
	008E4	8.02	5240	Light Yellow	>13w
REA-1167 #01	004E1	6.70		White	~5w
	004E2	7.14		↓	~9w
	004E3	7.47		↓	~23w
	004E4	7.96		Light Yellow	>23w

#### IV-2, 1K Alkyd Polyurethane Dispersions (PUDs)

The results obtained from one set of examples of PUDs are shown in Table 13, Figure 3 and Figure 4; and those from a further set of examples of PUDs are shown in Table 14, Figure 5 and Figure 6.

Experimental information:

(before reaction) PAD pH 6.78, visc. 90 CPS (original pH 7.16, visc. 330 CPS)

reaction time: after ~2 months

(after reaction) adjust to pH ~7.6 with 26%  $\text{NH}_3/\text{H}_2\text{O}$  respectively after 1 day.

Stability: Layer appearance time: PUD-07: ~11 weeks; PUD-08: ~13 weeks; all others >6 months.

Table 13

	PUD-I-1		PUD-I-2		PUD-I-3 :		PUD-I-4	
	PUD-07-1		PUD-08-1		PUD-09-1		PUD-10-1	
Date	261198		261198		261198		261198	
NVM%	42.00		42.85		44.42		45.85	
Original.PAD pH	7.16 (REA-1162-01-A001E721 Sept. 98; NVM% 38.3; Visc. cP330; Resin: AN 7.53; Color: 8)							
Keep time	~ 2 months (25 Nov. 98; NVM% 38.5; pH 6.78; Visc. cP90)							
Reaction.PAD pH	6.78		6.78		6.78		6.78	
After PUD process pH	6.94		6.95		7.23		7.19	
After overnight	6.30		6.17		6.42		6.58	
NH <sub>3</sub> H <sub>2</sub> O (26%)	0.45/100E		0.53/100E		0.38/100E		0.43/100E	
Days	pH	Visc.	pH	Visc.	pH	Visc.	pH	Visc.
0	7.60	78	7.59	84	7.65	146	7.80	328
8	7.33	94	7.59	106	6.95	180	7.14	634
11	7.60	100	7.69	108	7.69	168	7.62	632
14	7.67	98	7.78	106	7.71	172	7.97	656
21	7.68	92	7.84	104	8.05	170	8.15	626
35	7.70	94	7.82	102	8.04	166	8.16	612
42	7.82	92	7.88	100	8.58	164	8.32	610
49	7.89	88	7.93	106	8.71	176	8.41	640
56	7.9	88	7.98	98	8.57	164	8.39	612
63	8.01	88	8.47	98	8.53	160	8.56	560
77	7.92	94	8.39	100	8.49	160	8.70	530
91	8.11	80	8.62	94	8.75	148	8.89	456
105	8.03	60	8.57	72	8.65	110	8.84	396
119	8.11	72	8.58	80	8.51	114	8.84	420
133	8.05	64	8.39	70	8.32	102	8.75	380
147	7.98	68	8.31	72	8.28	110	8.68	446
161	7.91	70	8.18	78	8.19	128	8.65	490
175	7.79	72	8.01	72	8.06	120	8.54	464
189	7.84	70	8.01	70	8.07	116	8.47	464
Nole	~11 weeks can see layers		~13 weeks can see layers		>27 weeks		>27 weeks	

## Experimental information:

(before reaction) PAD pH 6.37, visc. 254 CPS (original pH 7.28, visc. 4170 CPS)

reaction time: >2 months

(after reaction) adjust to pH ~7.6 with 26% NH<sub>3</sub>/H<sub>2</sub>O respectively after 1 day.

Stability: Layer appearance time: PUD-12: ~19 weeks; all others >6 months.

Table 14

	PUD-II-1		PUD-II-2		PUD-II-3		PUD-II-4	
	PUD-12-1		PUD-13-1		PUD-14-1		PUD-15-1	
Date	011298		011298		011298		011298	
NVM%	42.95		44.35		46.18		47.39	
Original PAD pH	7.28 (REA-1165-01, A002E, 25 Sept 1998, NVM% 40.65, Visc. cP4170, Resin: AN, 12.81; Color: 13)							
Keep time	> 2 months (30 Nov 1998, NVM% 39.82, pH 6.37, Visc. cP254)							
Reaction PAD pH	6.37							
After PUD process pH	6.71		6.87		6.95		6.99	
After overnight	6.68		6.66		6.73		6.86	
NH <sub>3</sub> H <sub>2</sub> O (26%)	0.37/100E		0.32/100E		0.32/100E		0.25/100E	
Days	pH	Visc.	pH	Visc.	pH	Visc.	pH	Visc.
0	7.61	226	7.64	154	7.65	250	7.65	1120
3	7.51	246	7.53	170	7.42	238		
6	7.61	247	7.64	198	7.65	272	7.68	1162
9	7.6	314	7.86	210	7.65	272	7.60	1174
14	7.66	278	7.88	196	8.07	276	8.00	1212
28	7.77	286	7.84	174	8.15	272	8.31	1374
35	7.88	320	7.94	216	8.23	308	8.44	1440
42	7.84	358	8.02	224	8.18	294	8.47	1340
49	7.87	262	8.11	190	8.18	292	8.35	1240
56	7.82	252	8.25	184	8.17	280	8.42	1236
63	7.86	248	8.29	186	8.36	254	8.42	1220
74	7.88	238	8.17	166	8.58	264	8.78	1162
91	7.74	198	7.94	158	8.42	224	8.78	1032
105	7.67	204	8.01	162	8.24	242	8.70	1082
119	7.64	136	7.89	130	8.29	188	8.71	896
133	7.60	132	7.93	130	8.44	190	8.64	830
147	7.53	116	7.80	112	8.25	162	8.59	830
161	7.51		7.74		8.26		8.50	
175	7.41	108	7.65	104	8.31	144	8.37	830
180	7.45	92	7.62	104	8.25	144	8.22	830
Note	~19 weeks can see layers		>27 weeks		>27 weeks		>27 weeks	

A comparison of the appearance stability of PUD with PAD at room temperature is shown below in Table 15. This table lists the time when the deposition of PUD and PAD appeared.

**Table 15** Comparing the appearance stability of PUDs with PADs at room temperature:

Alkyd Dispersion (PADs)		Deposit appearance time			Polyurethane Dispersion (PUDs)		Deposit appearance (weeks)	
		1	2	3			1	3
REA-1162	#01/001E				PUD-I-1 PUD-I-2 PUD-I-3 PUD-I-4	PUD-07 PUD-08 PUD-09 PUD-10		~9w >19w >19w >19w
REA-1165	#01/002E				PUD-II-1 PUD-II-2 PUD-II-3 PUD-II-4	PUD-12-1 PUD-13-1 PUD-14-1 PUD-15-1		~19w >19w >19w >19w
	#03/008EB	<2w	<5w	>11w	PUD-II-1- PUD-II-2-	PUD-12-3 PUD-13-3	>11w >11w	
	#02/008EA	<3w	<5w	<6w	PUD-II-3-	PUD-14-3	<13w	
	#04/009EA	<2w	<9w	>9w		PUD-14-4	<7w	
	#06/013E-1	<1w	<2w	<6w		PUD-14-5-1	<2w	>6w
	#06/013E-2	<1w	<1w			PUD-14-5-2	~1w	~1w
	#06/013E-3	<1w	<1w			PUD-14-5-3	~1w	~1w
	#08/006EB-A	<3w	<3w	>3w		PUD-14-6-1	>3w	
	#08/006EB-B	<1w	<1w	<1w		PUD-14-6-2	>1w	>3w

1. Samples kept still at room temperature, appearance change monitored;
2. Stability test at room temperature, with no adjustment of pH every time;
3. Stability test at room temperature, with pH adjusted every time.

The products of the above examples were formulated with some additives to test their film properties.

## 1K PUD clear coat

1. A 1K PUD gloss clear coat was formulated based on alkyd polyurethane dispersion (PUD-II-1). The coating composition comprised the following ingredients:

Materials	Amount/g	
PUD-12-3	126.36	(PUD-II-1), NVM: 41.07
Servosyn Web Co.8%	0.99	
Active 8, 38%	0.29	
Butyl Cellosolve	15.0	
Exxol D-40	0.77	
Total	143.41	

The additives were added and mixed efficiently. The sample was then drawn on the substrate - glass, paper, wood, tin and aluminium, at a wet thickness of about 3mm. All panels were cured at room temperature for 7 days before being subjected to physical testing in accordance with the ASTM methods.

Coating characteristics and dry film properties are set out below:

Weight of solid %	36.9
Viscosity (s63, 60rpm)	476
Film appearance	Clear, glossy, soft and flexible
Gloss (glass, 60°) (ASTM D523)	173
Pencil Hardness (glass, scratch) (ASTM D3360)	HB
Sward Hardness (ASTM D2134)	24
Color, Yellowing	13.40
Dry Time: (ASTM D1640)	
Set to touch	30 min
Tack free	85 min
Thorough dry	100 min
Adhesion (A1 10x10, 1mm) (ASTM D3359)	100/100 passed
Bending Test (A1)	Crazing lines formed between clearance 5~15mm
Impact Test (ASTM G-14)	
Direct Impact	> 30 in-lbs
Indirect Impact	< 15 in-lbs

2. A 1K PUD low gloss clear coat was formulated based on alkyd polyurethane dispersion (PUD-II-3). The coating composition comprised the following ingredients:

Materials	Amount/g	
PUD-14-7	126.26	(PUD-II-3) NVM% 43.87
Servosyn Web Co.8%	1.04	
Active 8, 38%	0.31	
Butyl Cellosolve	15.3	
Exxol D-40	0.82	
Total	143.73	

The additives were added and mixed efficiently. The sample was then drawn on the substrate - glass, paper, wood, tin and aluminium, at a wet thickness of about 3mm. All panels were cured at room temperature for 7 days before being subjected to physical testing in accordance with the ASTM methods.

Coating characteristics and dry film properties are set out below:

Weight of solid %	36.9
Viscosity (s63,60rpm)	242
Film Appearance	Hazy, hard film
Gloss (glass 60°)	36.1
Pencil Hardness (glass, scratch)	F
Sward Hardness	10
Color, Yellowing	14.61
Dry Time:	
Set to touch	20
Tack free	30
Thorough dry	30
Adhesion (AI 10x10, 1mm)	100/100
Bending Test (AI)	Crazing at 0 T
Impact Test	
Direct Impact	>20 in-lbs
Indirect Impact	<5 in-lbs



3. A 1K PUD low gloss clear coat was formulated based on alkyd polyurethane dispersion (PUD-II-2). The coating composition comprises the following ingredients:

Materials	Amount/g	...
PUD-13-3	45.00	(PUD-II-2) NVM% 42.62
Servosyn Web Co.8%	0.353	
Active 8, 38%	0.10	
Butyl Cellosolve	5.29	
Exxol D-40	0.277	
Total	51.02	

The additives were added and mixed efficiently. The sample was then drawn on the substrate - glass, paper, wood, tin and aluminium, at a wet thickness of about 3mm. All panels were cured at room temperature for 7 days.

The film is clear, hard and flexible, and has a gloss appearance between those of examples 1 and 2 above.

#### 1K PUD White Paint

1. A 1K PUD white paint was formulated based on alkyd polyurethane dispersion (PUD-II-1,3). The formula and procedure are shown below:

	(PUD-II-1)PUD-12-3	(PUD-II-3)PUD-14-3
Materials	Amount/g	Amount/g
Grind Paste		
PUD	65.30	66.92
Dowanol DPM	6.62	7.36
Butyl Collosolve	13.27	14.74
Disperbyk 190	3.31	3.68
Surfynol DF-210	0.79	0.88
Ti-Pure R 902	66.29	73.66

Rinse		
Butyl Cellosolve	18.56	20.6
Exxol	1.67	1.86
Let-Down		
PUD	96.07	98.45
Final Additives		
Servosyn Web Zr 12%	1.06	1.18
Servosyn Web Co 8%	0.79	0.88
Butyl Cellosolve	1.33	1.47
Total	275.06	291.68

The additives were added and mixed efficiently. The sample was then reduced to a proper application viscosity with deionized (DI) water and drawn on the substrate - glass, paper, wood, tin and aluminium. All panels were cured at room temperature for 7 days before being subjected to physical testing in accordance with the ASTM methods.

Coating characteristics and dry film properties are set out below:

	(PUD-II-1) PUD-12-3	(PUD-II-3) PUD-14-3
Weight % Solid	50.3	49.3
Viscosity (KU)	93	90
pH	7.91	8.21
Dispersion (H)	6~7	6~7
Sag (ASTM D4400)	Clearance 8	Clearance 12
Gloss (ASTM D523)	62.5	64.2
Hiding (ASTM D2805)	Out of crytometer f 0.0005 range	Out of crytometer f 0.005 range
Pencil Hardness, (Wet film thickness 120 $\mu$ m)	HB	F
Yellowing	5.34	4.64

2. A 1K PUD white paint was formulated based on alkyd polyurethane dispersion (PUD-II-1). The formula and procedure are set out below:

	(PUDII-1)PUD-12-3	
	WD-PUD-12-DR-02	WD-PUD-12-DR-03
Materials	Amount/g	Amount/g
<b>Grind Paste</b>		
PUD12-3	65.30	65.30
Dowanol DPM	6.62	6.62
Butyl Cellosolve	13.27	13.27
Disperbyk 190	3.31	3.31
Surfynol DF-210	0.79	0.79
Ti Pure 706	66.29	
Ti-Pure 960		66.29
<b>Rinse</b>		
Butyl Cellosolve	18.56	18.56
Exxol D-40	1.67	1.67
<b>Let-Down</b>		
PUD-12-3	96.07	96.07
<b>Final Additives</b>		
Servosyn Web Zr 12%	1.06	1.06
Servosyn Web Co 8%	0.79	0.79
Butyl Cellosolve	1.33	1.33
<b>Total</b>	<b>275.06</b>	<b>275.06</b>

The additives were added and mixed efficiently. The sample was then reduced to a proper application viscosity with de-ionised water and drawn on the substrate - glass, paper, wood, tin and aluminium. All panels were cured at room temperature for 7 days before being subjected to physical testing in accordance with the ASTM methods.

Coating characteristics and dry film properties are set out below:

	WD-PUD-12-DR-02	WD-PUD-12-DR-03
Weight % Solid	50	49.5
Viscosity (Krebs units, KU)	93	90
Dispersion (H)	7	7
Sag	Clearance:10	Clearance: 6
Gloss, 60° (3mm on paper)	90	55.9
Pencil Hardness,	F	F
(Wet film thickness 3mil)		
Yellowing (3mil on paper)	3.23	3.24

3. A 1K PUD white paint was formulated based on alkyd polyurethane dispersion (PUD-II-3). The formula and procedure are set out below:

	(PUDII-3)PUD-14-3	
	WD-PUD-14-DR-03	WD-PUD-14-DR-04
Materials	Amount/g	Amount/g
<b>Grind Paste</b>		
PUD14-3	66.92	66.92
Dowanol DPM	7.36	7.36
Butyl Cellosolve	14.74	14.74
Disperbyk 190	3.68	3.68
Surfynol DF-210	0.88	0.88
Ti Pure 706	73.66	
Ti-Pure 960		73.66
<b>Rinse</b>		
Butyl Cellosolve	20.6	20.6
Exxol D-40	1.87	1.86
<b>Let-Down</b>		
PUD-14-3	98.45	98.45
<b>Final Additives</b>		
Servosyn Web Zr 12%	1.18	1.18
Servosyn Web Co 8%	0.88	0.88
Butyl Cellosolve	1.47	1.47
<b>Total</b>	<b>291.68</b>	<b>291.67</b>

The additives were added and mixed efficiently. The sample was then reduced to a proper application viscosity with DI water and drawn on the substrate - glass, paper, wood, tin and aluminium. All panels were cured at room temperature for 7 days before being subjected to physical testing in accordance with the ASTM methods.

Coating characteristics and dry film properties are set out below:

	WD-PUD-14-DR-03	WD-PUD-14-DR-04
Weight % Solid	46.1	47.7
Viscosity (KU)	90	91
Dispersion (H)	7	7
Sag	Clearance >26 mm	Clearance >26mm
Gloss, 60° (3mm on paper)	67.1	42.4
Pencil Hardness,	F	F
(Wet film thickness 3mil)		
Yellowing (3mil on paper)	3.24	3.24

Low VOC waterborne alkyd 2K polyurethane.

A 2K high gloss varnish was formulated based on polyol alkyd dispersion. The crosslinker for the system was RHODOCOAT WT-2102, an aliphatic polyisocyanate from CRHODIA. The ratio of NCO/OH was 1.1/1.

Two-component low VOC waterborne PU Clearcoat based on polyol alkyd dispersion and RHODOCOAT WT-2101. The starting formulation is below:

	Ingredients	Weight %
Part 1	REA-1165-09	71.53
	{NVM% 38.52, Eq.wt.(OH): 298g (solid)}	
	Surfynol 465	0.19
	DI water	7.45
	BYK307	0.07
	BYK011	0.10
	BYK348	0.35
Part 2	RHODOCOAT WT 2102	20.28

The part 1 and part 2 were added and hand mixed. The sample were then reduced to a proper application viscosity (62 Kus) with DI water and drawn on Q panels for testing. All panels were cured at room temperature for 7 days before being subjected to the physical testing in accordance with the ASTM methods.

## Coating Characteristics and Dry Film Properties.

Weight % Solid (Part 1/Part 2)	39.59
Viscosity	62 Kus
VOC (gram/liter)	<50g/liter
Impact-Direct (inch/lbs)	80
Mandrel testing (ASTM D522-88)	Pass 1/8 inch
Pencil Hardness	H
Gloss 20°/60°	83.7/91.8
Crosshatch Adhesion (ASTM D3359)	5B
Dry time (1.8 mm DFT)	10 hours
MEK Double rubs (ASTM D4752)	100+

In this specification the term "comprising" means "including or consisting of" and the term "comprises" means "includes or consists of".

The features disclosed in the foregoing description, or the following claims, or the accompanying drawings, expressed in their specific forms or in terms of a means for performing the disclosed function, or a method or process for attaining the disclosed result, as appropriate, may, separately, or in any combination of such features, be utilised for realising the invention in diverse forms thereof.

CLAIMS:

1. A method of making a polyol alkyd resin comprising an alcoholysis step of reacting polyethylene glycol (PEG), an oil and a polyhydric alcohol; followed by an esterification step of reacting the resultant mixture from the alcoholysis step with an acid and/or an acid anhydride, and a polyhydroxy compound with the esterification step being terminated on reaching a predetermined acid value or predetermined viscosity.
2. A method according to Claim 1 wherein the oil is safflower oil.
3. A method according to Claim 2 wherein the oil is soybean oil.
4. A method according to any one of the preceding claims wherein the polyhydric alcohol and/or the polyhydroxy compound is pentaerythritol.
5. A method according to any one of the preceding claims wherein the acid is p-t-butyl benzoic acid or benzoic acid.
6. A method according to any one of Claims 1 to 4 wherein the acid is, and/or the acid anhydride corresponds to, a polybasic acid.
7. A method according to Claim 6 wherein the acid is isophthalic acid.
8. A method according to Claim 6 or Claim 7 wherein the acid anhydride is phthalic anhydride.
9. A method according to any one of the preceding claims wherein the PEG has a molecular weight in the range of 3000-3700.

10. A polyol alkyd resin made according to the method of any one of Claims 1 to 9, or a method equivalent thereto.

11. A method of making an aqueous polyol alkyd resin dispersion, (PAD), comprising the steps of heating in a reactor a predetermined amount of water, and a predetermined amount of an amine, to a dispersing temperature, and pouring into the reactor, with stirring, a polyol alkyd resin, which has been heated to a melt state, at such a rate that the temperature of the mix in the reactor is no more than about 5°C above the dispersing temperature, with the temperature in the reactor being held at about the dispersing temperature for a period of time after the addition of the resin.

12. A method according to Claim 11 further comprising the steps of cooling the mix to room temperature and adjusting the pH and/or solids content of the dispersion.

13. A method according to Claim 11 or Claim 12 wherein the amine is triethylamine, 2-amino-2-methyl-1-propanol, dimethylethanol amine (DMEA), or ammonia solution.

14. A method according to any one of Claims 11, 12 or 13 wherein the dispersing temperature is in the range of 55°-70°C.

15. A method according to any one of Claims 11 to 14 wherein the dispersing temperature is in the range of 60°-65°C.



16. A method according to any one of Claims 11 to 15 wherein the amine is added in a mole ratio amount in the range of 0.3-1.0:1.0 with respect to the resin.

17. A method according to Claim 16 wherein the amine is added in a mole ratio amount in the range of 0.6-0.95:1.0 with respect to the resin.

18. A method according to any one of Claims 11 to 17 wherein the solids content of the dispersion is in the range of 35-45%.

19. A method according to any one of Claims 11 to 18 wherein the solids content of the dispersion is in the range of 38-40%.

20. An aqueous polyol alkyd resin dispersion, (PAD), made according to the method of any one of Claims 11 to 19.

21. A method of making an aqueous polyurethane dispersion (PUD) from a polyol alkyd dispersion (PAD) comprising the steps of heating in a reactor a predetermined amount of water, and a predetermined amount of an amine, to a dispersing temperature, and pouring into the reactor, with stirring, a polyol alkyd resin, which has been heated to a melt state, at such a rate that the temperature of the mix in the reactor is no more than about 5°C above the dispersing temperature, with the temperature in the reactor being held at about the dispersing temperature for a period of time after the addition of the resin, followed by reaction with an isocyanate chain extender..

22. A method according to Claim 21 further comprising the steps of cooling the mix to room temperature and adjusting the pH and/or solids content of the dispersion.

23. A method according to Claim 21 or Claim 22 wherein the amine is triethylamine, 2-amino-2-methyl-1-propanol, dimethylethanol amine (DMEA), or ammonia solution.

24. A method according to any one of Claims 21, 22 or 23 wherein the dispersing temperature is in the range of 55°-70°C.

25. A method according to any one of Claims 21 to 24 wherein the dispersing temperature is in the range of 60°-65°C.

26. A method according to any one of Claims 21 to 25 wherein the amine is added in a mole ratio amount in the range of 0.3-1.0:1.0 with respect to the resin.

27. A method according to Claim 26 wherein the amine is added in a mole ratio amount in the range of 0.6-0.95:1.0 with respect to the resin.

28. A method according to any one of Claims 21 to 27 wherein the solids content of the dispersion is in the range of 35-45%.

29. A method according to any one of Claims 21 to 28 wherein the solids content of the dispersion is in the range of 38-40%.

30. A method according to any one of Claims 21 to 29 wherein the chain extender is an isocyanate-containing compound.

31. A method according to any one of Claim 30 wherein the isocyanate-containing compound is an aliphatic compound.

32. A method according to Claim 30 or 31 wherein the isocyanate-containing compound is isophorone di-isocyanate.

33. A method according to Claim 30 wherein the isocyanate-containing compound is an aromatic compound.

34. A method according to any one of Claims 30 to 33 wherein the isocyanate containing compound is a di-isocyanate.

35. A method according to any one of Claims 21 to 29 wherein the chain extender is an aziridine-containing compound.

36. A method according to any one of Claims 21 to 35 wherein the range of equivalents of the chain extender to the solids content of the polyol alkyd dispersion is in the range of between 10:90 and 30:70.

37. A method according to any one of Claims 21 to 36 wherein the range of equivalents of the chain extender to the solids content of the polyol alkyd dispersion is in the range of between 10:90 and 20:80.

38. A method according to any one of Claims 21 to 37 wherein the range of equivalents of the crosslinker to the solids content of the polyol alkyd dispersion is about 15:85.

39. A method according to any one of Claims 21 to 38 wherein the reaction is performed in the temperature range of from about 25° to about 30°C.

40. An aqueous polyurethane dispersion, (PUD), made according to the method of any one of Claims 21 to 39, or a method equivalent thereto.

41. A one component (1K) coating system comprising the dispersion of Claim 20, or a two component (2K) coating system comprising the dispersion of Claim 40.

42. A coating system according to Claim 41 wherein the coating system is a room-temperature cure or a baking-type coating system.

43. A film made from the dispersion of Claim 20 or 40.

44. Any novel feature or combination of features disclosed herein.

## AMENDED CLAIMS

[received by the International Bureau on 15 March 2002 (15.03.02);  
original claims 1-44 replaced by new claims 1-46 (6 pages)]

- 1 A method of making a solvent-free polyol alkyd resin comprising an alcoholysis and emulsifying re-arrangement step of reacting polyethylene glycol (PEG), an oil and a polyhydric alcohol, followed by an esterification step of reacting the resultant mixture from the alcoholysis and emulsifying re-arrangement step with an acid and/or a acid anhydride, and a polyhydroxy compound with esterification step being terminated on reaching a predetermined acid value or predetermined viscosity.
- 2 A method according to Claim 1 wherein the first process of the synthesis is an alcoholysis and emulsifying re-arrangement step.
- 3 A method according to Claim 1 wherein the oil content in the alkyd resin is less then 40% in solid.
- 4 A method according to Claim 1 wherein the acid number of the alkyd resin lies between 12 to 25.
- 5 A method according to Claim 1 wherein the molecular weight of the alkyd resin is between 3,000 to 14,000.
- 6 A method according to Claim 1 wherein the quantity of organic solvent in the process is controlled so that the solvent content of the product is zero by weight.
- 7 A method according to any one of the preceding claims wherein the PEG has a molecular

weight in the range of 3000-3700.

- 8 A solvent-free polyol alkyd resin made according to the method of any of Claims 1 to 7, or a method equivalent thereto.
- 9 A method of making an aqueous solvent-free polyol alkyd resin dispersion, (PAD), comprising the steps of heating in a reactor a predetermined amount of water, and predetermined amount of an amine, to a dispersing temperature, and pouring into the reactor, with stirring, a polyol alkyd resin, which has been heated to a melt state, at such a rate that the temperature of the mix in the reactor is no more than about 5 °C, above the dispersing temperature, with the temperature in the reactor being held at about the dispersing temperature for a period of time after the addition of the resin.
- 10 A method according to Claim 9 wherein the alkyd resin used to process dispersing is PEG modified, low oil content and solvent-free.
- 11 A method according to Claim 9 further comprising there is no external surfactant/or and solubilizer or and emulsifier added in the dispersing process.
- 12 A method according to Claim 9 further comprising there is no co-solvent added in the dispersing process.
- 13 A method according to Claims 9, 10, 11 or 12 wherein the dispersing temperature is in the range of 55°-70 °C.

- 14 A method according to Claims 9 to 13 wherein the dispersing temperature is in the range of 60°-65 °C.
- 15 A method according to any one of Claims 9 to 14 wherein amine is added in a mole ratio amount in the range of 0.3-1.0:1.0 with respect to the resin.
- 16 A method according to any one of Claims 15 wherein amine is added in a mole ratio amount in the range of 0.6-0.95:1.0 with respect to the resin.
- 17 A method according to any one of Claims 9 to 16 wherein the solid content of the dispersion is in the range of 35-45%.
- 18 A method according to any one of Claims 9 to 17 wherein the solid content of the dispersion is in the range of 38-40%.
- 19 An aqueous solvent-free polyol alkyd resin dispersion, (PAD), made according to the method of any one of Claims 9 to 18.
- 20 A method of making an aqueous solvent-free polyurethane dispersion (PUD) from a solvent-free polyol alkyd dispersion (PAD) comprising the steps of heating in a reactor a predetermined amount of water, and a predetermined amount of an amine, to a dispersing temperature, and pouring into the reactor, with stirring, a polyol alkyd resin, which has been heated to a melt state, at such a rate that the temperature of the mix in the reactor is no more than about 5°C above the dispersing temperature, with the temperature in the reactor being held at about the dispersing temperature for a period of time after the addition of the resin, followed by reaction with isocyanate chain extender.
- 21 A method according to Claim 20 further comprising the urethane reaction is carried on after dispersing process.
- 22 A method according to Claim 20 further comprising there is no external surfactant/or and solubilizer or and emulsifier added in the dispersion.

- 23 A method according to Claim 20 further comprising there is no co-solvent added in the dispersion.
- 24 A method according to Claims 20 further comprising the steps of cooling the mix to room temperature and adjusting the pH and /or solid content of the dispersion.
- 25 A method according to Claim 20 or Claim 24 wherein the amine is **Triethylamine, Dimethylethanol amine (DMEA) or ammonia solution.**
- 26 A method according to any one of Claims 20, 24 or 25 wherein the dispersing temperature is in the range of 55°-70°C.
- 27 A method according to any one of Claims 20 to 26 wherein the dispersing temperature is in the range of 60°-65°C.
- 28 A method according to any one of Claims 20 to 27 wherein the amine is added in a mole ratio amount in the range of 0.3-1.0:1.0 with respect to the resin.
- 29 A method according to Claims 28 wherein the amine is added in a mole ratio amount in the range of 0.6-0.95:1.0 with respect to the resin.
- 30 A method according to any one of Claims 20-29 wherein the solids content of the dispersion is in the range of 35-45%.
- 31 A method according to any one of Claims 20-30 wherein the solids content of the dispersion is in the range of 38-40%.
- 32 A method according to any one of Claims 20-31 wherein the chain extender is an isocyanate-containing compound.
- 33 A method according to any one of Claims 32 wherein the isocyanate-containing compound is an aliphatic compound.



- 34 A method according to any one of Claims 32 to 33 wherein the isocyanate-containing compound is isophorone di-isocyanate.
- 35 A method according to any one of Claims 32 wherein the isocyanate-containing compound is an aromatic compound.
- 36 A method according to any one of Claims 32 to 35 wherein the isocyanate containing compound is a di-isocyanate.
- 37 A method according to any one of Claims 20-31 wherein the chain extender is an aziridine-containing compound.
- 38 A method according to any one of Claims 20 to 37 wherein the range of equivalents of the chain extender to the solids content of the polyol alkyd dispersion is in the range of between 10:90 and 30:70.
- 39 A method according to any one of Claims 20 to 38 wherein the range of equivalents of the chain extender to the solids content of the polyol alkyd dispersion is in the range of between 10:90 and 20:80.
- 40 A method according to any one of Claims 20 to 39 wherein the range of equivalents of the chain extender to the solids content of the polyol alkyd dispersion is about 15:85.
- 41 A method according to any one of Claims 20 to 40 wherein the reaction is performed in the temperature range of from about 25° to about 30°C.
- 42 A aqueous solvent-free polyurethane dispersion, (PUD), made according to the method of any one of Claims 20 to 41, or a method equivalent thereto.
- 43 A one component (1K) coating system comprising the dispersion of Claim 19, or two component (2K) coating system comprising the dispersion of Claim 41.
- 44 A coating system according to Claim 43 wherein the coating system is a room-

temperature cure or a baking-type coating system.

45 A film made from the dispersion of Claim 19 or 42.

46 Any novel feature or combination of features disclosed herein.

1/3

Stability of viscosity as time increased  
(REA-1165-02)

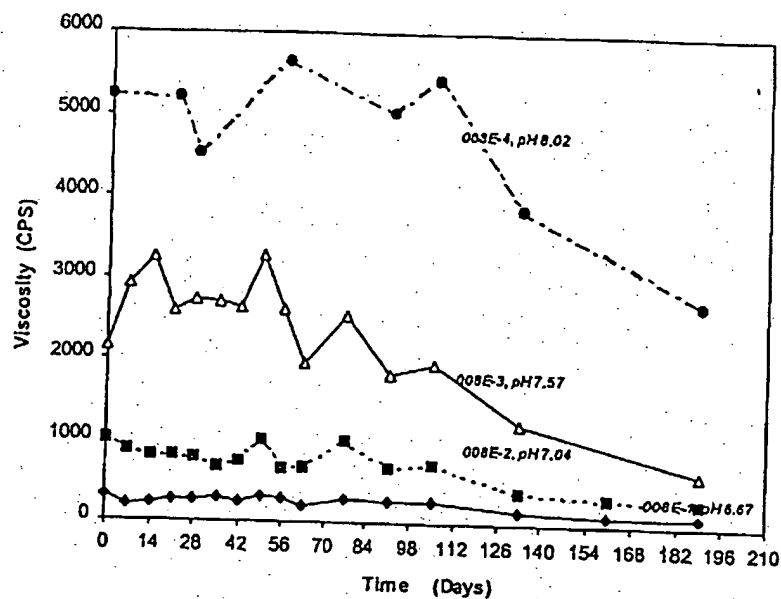


Figure 1

Viscosity change as time increased  
(REA-1165-02)

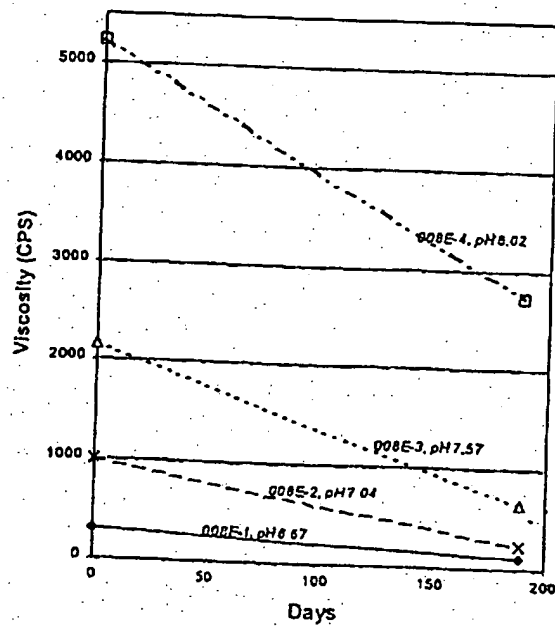


Figure 2

2/3

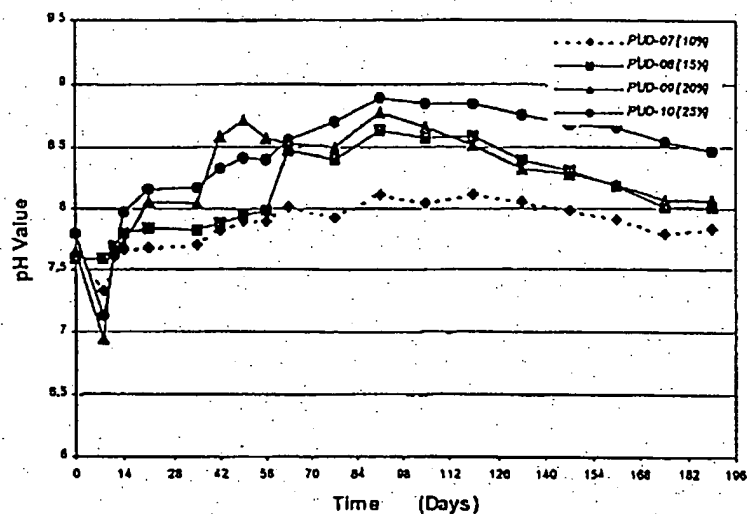
Change in pH over six months  
(PUD-07, 08, 09, 10)

Figure 3

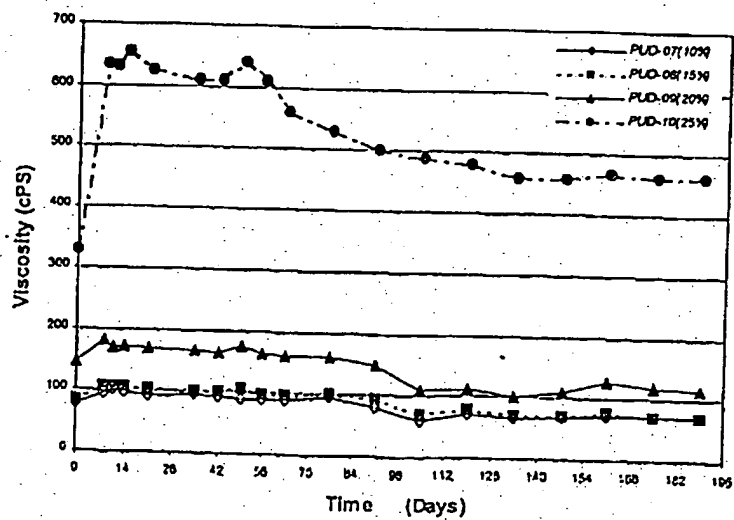
Change in Viscosity over six months  
(PUD-07, 08, 09, 10)

Figure 4

3/3

Change in pH over six months  
(PUD-12, 13, 14, 15-1)

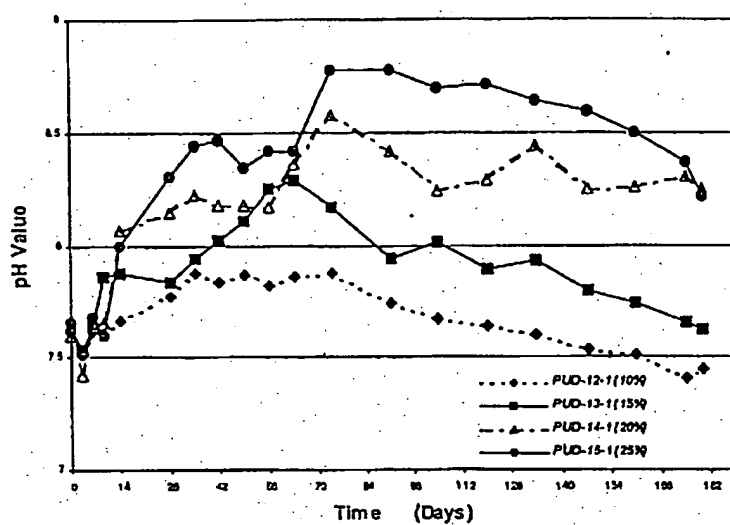


Figure 5

Change in viscosity over six months  
(PUD-12, 13, 14, 15-1)

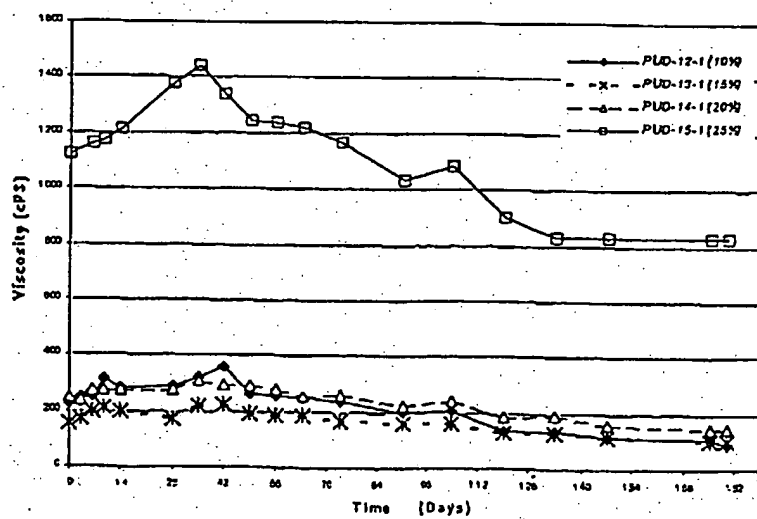


Figure 6

## INTERNATIONAL SEARCH REPORT

International Application No.  
PCT/SG 01/00192

## CLASSIFICATION OF SUBJECT MATTER

IPC<sup>7</sup>: C08G 63/49, 63/91, 18/42

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC<sup>7</sup>: C08G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

DEPATISNET, EPODOC, WPI, PAJ

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	GB 896743 A (WILLEM DORST) 16 May 1962 (16.05.62) <i>example 3, claim 1, page 2, lines 3-64.</i>	1,3,4,7,10-13, 20
Y		2,5,6,21,30-34, 40-43
Y	US 5004779 A (BLUM et al.) 2 April 1991 (02.04.91) <i>claims, column 3, line 21 - column 4, line 21, column 5, lines 3-49.</i>	2,5,6,21,30-34, 40-43
A		1,3,4,7,8,10,11 , 13,20
X	DD 299467 A7 (LACKHARZ ZWICKAU GMBH) 23 April 1992 (23.04.92) <i>claim, examples.</i>	1,3,6,8,10
A	WO 88/03153 A1 (BASF LACKE + FARBEN AG) 5 May 1988 (05.05.88) <i>claims 4-9, page 4, line 28 - page 5, line 24.</i>	1,3-6,8,10,21, 30-34

☒ Further documents are listed in the continuation of Box C.☒ See patent family annex.

\* Special categories of cited documents:

..A.. document defining the general state of the art which is not considered to be of particular relevance

..B.. earlier application or patent but published on or after the international filing date

..C.. document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

..D.. document referring to an oral disclosure, use, exhibition or other means

..E.. document published prior to the international filing date but later than the priority date claimed

..T.. later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

..X.. document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

..Y.. document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

..R.. document member of the same patent family

Date of the actual completion of the international search

13 December 2001 (13.12.2001)

Date of mailing of the international search report

17 January 2002 (17.01.2002)

Name and mailing address of the ISA/AT

Austrian Patent Office  
Kohlmarkt 8-10; A-1014 Vienna

Facsimile No. 1/53424/535

Authorized officer

WEIGERSTORFER

Telephone No. 1/53424/221

## INTERNATIONAL SEARCH REPORT

International application No.

PCT/SG 01/00192

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP 58 052370 A (DAINIPPON TORYO K.K.) 28 March 1983 (28.03.83) (abstract). [online] [retrieved on 2001-12-13]. Retrieved from: EPOQUE PAJ Database.	11,13,20,21,23 , 30,40

# INTERNATIONAL SEARCH REPORT

International application No.  
PCT/SG 01/00192

## Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:  
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☒ Claims Nos.: 44  
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:  
Claim 44 is unclear so that no meaningful search can be carried out.
3. ☐ Claims Nos.:  
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

## Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

### Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest.  
☐ No protest accompanied the payment of additional search fees.



# INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/SG 01/00192

Patent document cited in search report			Publication date	Patent family member(s)		Publication date
DD	A	299467		none		
GB	A	896743		none		
JP	A2	58052370	28-03-1983	JP	B4	62020232
US	A	5004779	02-04-1991	AT	B	95542
				CA	AA	2007751
				DE	A1	3902190
				DE	C6	59002957
				EP	A2	379007
				EP	A3	379007
				EP	B1	379007
				ES	T3	2046534
				JP	A2	2258823
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				DE	A1	3636929
				EP	A1	265746
				EP	A1	321502